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(56) Reference Literatures:
            Japanese Laid-open Patent Publication
                No. 58(1983)-19309 (JP, A)
            Japanese Laid-open Patent Publication
                No. 60(1985)-35007 (JP, A)

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Propylene random copolymers and heat-sealing modifier

for thermoplastic resins containing the same

[CLAIMS]

1.   A propylene random copolymer comprising a propylene

component and an α-olefin component having 4 to 12 carbon

atoms, characterized in that;

A)   the composition is 40 to 90 mol % of the propylene

component and 10 to 60 mol % of the α-olefin component;

B)   the intrinsic viscosity [η] when measured in decalin

at 135°C is in the range of 0.5 to 6 dl/g;

C)   the molecular weight distribution ($\overline{Mw}/\overline{Mn}$) when measured

by gel-permeation chromatography (GPC) is in the range of 3

or below;

D)   the melting point [Tm] measured with a differential

scanning calorimeter is in the range of 40 to 140°C;

E)   the crystallinity measured with a differential scanning

calorimeter is in the range of 1 to 50%;

F)   the content [W_1 wt%] of a component soluble in boiling

methyl acetate is in the range of 1 wt% or below;

G)   the content [W_2 wt%] of a component soluble in a mix-

ture solvent of acetone and n-decane (volume ratio 1/1) at

10°C is in the range of 4 X [η]$^{-1.2}$ wt% or below;

H)   no signal based on two consecutive methylene chains is

observed between two adjacent tertiary carbon atoms in the

main chain of the copolymer in the ^{13}C-NMR spectrum of the

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copolymer; and

I) the standard deviation of the composition distribution in the copolymer is in the range of 10 mol% or below.

2. A heat-sealing modifier for thermoplastic resins containing a propylene random copolymer comprising a propylene component and an α-olefin component having 4 to 12 carbon atoms, the propylene random copolymer characterized in that;

A) the composition is 40 to 90 mol % of the propylene component and 10 to 60 mol % of the α-olefin component;

B) the intrinsic viscosity [η] when measured in decalin at 135°C is in the range of 0.5 to 6 dl/g;

C) the molecular weight distribution ($\overline{M}w/\overline{M}n$) when measured by gel-permeation chromatography (GPC) is in the range of 3 or below;

D) the melting point [Tm] measured with a differential scanning calorimeter is in the range of 40 to 140°C;

E) the crystallinity measured with a differential scanning calorimeter is in the range of 1 to 50%;

F) the content [W_1 wt%] of a component soluble in boiling methyl acetate is in the range of 1 wt% or below;

G) the content [W_2 wt%] of a component soluble in a mixture solvent of acetone and n-decane (volume ratio 1/1) at 10°C is in the range of 4 X [η]$^{-1.2}$ wt% or below;

H) no signal based on two consecutive methylene chains is observed between two adjacent tertiary carbon atoms in the

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main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer; and

I) the standard deviation of the composition distribution in the copolymer is in the range of 10 mol% or below.

[Detailed Description of the Invention]

[Industrially Applicable Field]

The present invention relates to a novel propylene random copolymer. More particularly, the present invention relates to a propylene random copolymer having a narrow molecular weight distribution and a narrow composition distribution and being excellent in transparency, surface non-adhesiveness, tensile strength, and other properties; for example, a propylene random copolymer suitable for forming a film for wrapping, a sheet-like product, and other molten forms excellent in transparency, blocking resistance, and others. Also the present invention relates to a modifier for thermoplastic resins excellent in improving heat-sealing property and impact resistance by mixing with a thermoplastic resin such as an olefin copolymer.

[Prior Art]

Conventionally, in the application field of soft or semi-hard resin, the use of vinyl chloride resin was prevalent. However, conversion into olefin type soft or semi-hard resins is now desired due to problems of corrosive gas generation at the time of waste incineration and doubtful

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safety of residual monomers and plasticizers. Therefore, there is an increasing need for α-olefin type soft copolymers for use in the field of molding or as a modifier for various kinds of resins.

As the α-olefin soft copolymer, a copolymer of more than two kinds of α-olefins is generally known. As the method for manufacturing the same, a method is known in which two or more kinds of α-olefins are copolymerized under the presence of a titanium-type catalyst containing a titanium compound and an organoaluminum compound or a vanadium-type catalyst containing a vanadium compound and an organoaluminum compound. The α-olefin type soft copolymers obtained by using a titanium-type catalyst are generally inferior in random copolymerizing property, have wide molecular weight distribution and wide composition distribution, and are inferior in transparency, surface non-adhesiveness and mechanical properties. On the other hand, the α-olefin type soft copolymers obtained by using a vanadium-type catalyst generally have ethylene content of 50 mol% or more and have improved random property, narrower molecular weight distribution, narrower composition distribution, and considerably improved transparency, surface non-adhesiveness and mechanical properties when compared with those obtained by using a titanium-type catalyst. Still, they are not suitable enough for use which severely requires these properties, so that there is a need for α-olefin type soft copoly-

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mers with these properties further improved.

The olefin-type resins that are recently used in the application field of molding soft or semi-hard resin include olefin copolymers such as ethylene copolymers, propylene copolymers, and 1-butene-type copolymers. Among these olefin-type soft or semihard resins, for soft 1-butene random copolymers containing 1-butene as a major component and propylene, there are numerous proposals. USP No. 3,278,504, USP No.3,332,921, USP No.4,168,361, and British Patent No.1,018,341 disclose 1-butene random copolymers manufactured by using titanium trichloride or titanium tetrachloride catalyst. However, these 1-butene random copolymers, in common, have a high content of low molecule polymer components such as a component soluble in boiling methyl acetate or a component soluble in a mixture solvent of acetone and n-decane (volume ratio 1/1), and they have a wide composition distribution and a molecular weight distribution. Therefore, the molded articles, especially films or sheets, formed of these 1-butene-type random copolymers have high surface adhesiveness and considerable blocking properties. Also, most of them have low random properties and are inferior in transparency, so that it was not possible to obtain formed article having high commercial values.

The above-mentioned USP No.3,278,504 proposes a propylene · 1-butene copolymer having a 1-butene content in the

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range of 30 to 70 mol%. It is disclosed therein that the 1-butene type copolymer is manufactured by using titanium tetrachloride or titanium trichloride. However, the copolymers manufactured by using these catalyst systems are soft resins with the content of the component soluble in boiling methyl acetate being more than 2 wt%, the content of the component soluble in a mixture solvent of acetone and n-decane (volume ratio 1/1) being high, and having surface adhesiveness and inferior transparency.

The above-mentioned USP No. 3,332,921 and British Patent No. 1,084,953 propose various kinds of 1-butene copolymers manufactured by using a titanium trichloride catalyst with varying content of 1-butene. Among these copolymers, the 1-butene-type copolymers having a 1-butene content in the range of 60 to 99 mol% have similar properties to the 1-butene type copolymers proposed in the above-mentioned USP No.3,278,504.

According to the above-mentioned British Patent No. 1018314, a copolymer having a 1-butene content in the range of 25 to 90 mol% is obtained by using a transition metal halide such as titanium trichloride and a derivative of phosphoric acid in combination. Among the copolymers specifically disclosed in the proposal, with respect to the 1-butene copolymers having a 1-butene content in the range of 50 to 90 mol%, the disclosure is directed to only the copolymers which contain 1.5 wt% or more of the component soluble

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in acetone. By examination of the inventors of the present application, it has been found out that, in these copolymers, the ratio of the component soluble in boiling methyl acetate is high, and the ratio of the component soluble in a mixture solvent of acetone and n-decane (volume ratio 1/1) is more than $5 \times [\eta]^{-1.2}$ wt%, so that, from the 1-butene type copolymers, only formed articles having a high surface adhesiveness and inferior transparency can be obtained.

Further, the above-mentioned USP No.4,168,361 discloses propylene · 1-butene copolymers in which the content of propylene is in the range of 40 to 90 mol%. However, among these copolymers, it has been found out by the examination of the inventors of the present application that, also in these copolymers in which the content of propylene is in the range of 50 to 60 mol%, the ratio of the component soluble in a mixture solvent of acetone and n-decane is high, so that, from the 1-butene type copolymers, it is possible to obtain only formed articles having a high surface adhesiveness and inferior transparency.

On the other hand, in Japanese Unexamined Patent Publication (Kokai) No. Sho 50(1975)-38787, there is proposed a method for conducting a polymerization at a high temperature by using a titanium trichloride catalyst so as to obtain a non-chrystalline random copolymer.

Examination by the inventors of the present application

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has revealed that, according to this method, the obtained copolymer has a high content of the component soluble in methyl acetate and is inferior in tensile strength, so that it cannot be used for resin.

Also, the present applicant proposed, in Japanese Unexamined Patent Publication (Kokai) No. Sho 54(1979)-85293, a 1-butene · propylene random copolymer containing 1-butene as a major component which has a narrow composition distribution, a low content of the component soluble in boiling methyl acetate, and small surface adhesiveness. In the 1-butene · propylene copolymer provided by this proposal, the content of low-molecular-weight component, especially the content represented by the component soluble in boiling methyl acetate, and the surface-adhesiveness of articles formed of the copolymer are surely much improved compared with conventional ones, but disadvantageously, the molecular weight distribution ($\overline{M}w/\overline{M}n$), 3.6, of the 1-butene · propylene random copolymer is not sufficiently narrow; the content of low-molecular-weight components, especially represented by the component soluble in the mixture solvent of acenton · n-decane (volume ratio 1/1), is still high; and the surface adhesiveness of formed articles, e.g., films, of polypropylene resin blended with the 1-butene · propylene random copolymer as impact resistance enhancer tends to increase with time. The 1-butene · propylene random copolymer cannot be considered suitable enough for use in fields

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requiring excellency in surface non-adhesiveness and trans-
parency. Further the 1-butene · propylene random copolymer
by this proposal is of low crystallinity and poor in mechan-
ical properties such as rigidity. Therefore, it cannot be
considered sufficient for use in fields requiring excellent
mechanical properties.

As a new Ziegler olefin polymerization catalyst differ-
ent from conventionally known titanium and vanadium cata-
lysts, Japanese Unexamined Patent Publication Nos. Sho
58(1983)-19309, Sho 59(1984)-952925, Sho 60(1985)-35005, Sho
60(1985)-35006, Sho 60(1985)-35007 and Sho 60(1985)-35009
propose catalysts of zirconium compound and aluminoxane .
In these prior-art literatures, copolymers of two or more
α-olefins are described. For example, in example 7 of Sho
58(1983)-19309, examples to 3 of Sho 60(1985)-35006, and
examples 10 and 11 of Sho 60(1985)-35007, ethylene · α-
olefin copolymers are disclosed. However, all these ethyl-
ene · α-olefin copolymers have wide molecular weight distri-
bution and composition distribution, or most of them are
insufficient in performance such as transparency, surface
non-adhesiveness and mechanical properties for use in their
usage fields. Therefore, there is a demand for an α-olefin
soft copolymer of such performance improved.

The applicant also proposed soft low-crystalline pro-
pylene copolymers containing propylene by copolymerizing pro-

pylene and α-olefin other than propylene in Japanese Unexamined Patent Publication Nos. Sho 52(1977)-19153, Sho 55(1980)-118909, Sho 55(1980)118910, Sho 53(1978)-79984, Sho 53(1978)-104686, Sho 54(1979)-85293 and Sho 60(1985)-38414. These soft low-crystalline propylene copolymers contain less of the component soluble in boiling methyl acetate than conventional soft low-crystalline propylene copolymers do, have been improved in surface non-adhesiveness, blocking properties and transparency. However, they still cannot be considered suitable enough for use in fields requiring such properties more definitely. Furthermore, all the copolymers obtained by the above methods have wide molecular weight distribution. Therefore, there is a strong demand for a soft low-crystalline propylene copolymer with the aforesaid properties further improved for application in fields requiring the definite properties.

[Problems to be Solved by the Invention]

The present inventors recognized that the conventional propylene random copolymers have wide molecular weight distribution and contain a lot of low-molecular-weight polymers and that formed articles obtained with the conventional propylene random copolymers are poor in surface non-adhesiveness, transparency and mechanical properties such as rigidity. And the inventors have been making keen study with a view to providing a propylene random copolymer with

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these properties improved over the conventional propylene random copolymers.

As a result, the inventors have found that a propylene random copolymer can exist which comprises propylene as major component and an α-olefin having 4 to 12 carbon atoms and is characterized by the properties defined by the later-described (A) to (I) and which have not been seen in any conventionally known literatures, and have succeeded in synthesizing the same.

The inventors have further found that the novel propylene random copolymer has narrower molecular weight distribution and contains less low-molecular-weight components, especially represented by the components soluble in boiling methyl acetate and in the mixture solvent of acetone • n-decane (volume ratio of 1 : 1), compared with the conventionally known propylene random copolymer, and that articles formed of the propylene random copolymer are especially excellent in surface non-adhesiveness, transparency and mechanical properties such as rigidity.

Accordingly, a purpose of the invention is to provide a new propylene random copolymer comprising a propylene component and an α-olefin component having 4 to 12 carbon atoms.

Another purpose of the invention is to provide a modifier for thermoplastic resins which is added to a thermoplastic resin such as olefin copolymer to improve heat-sealing properties or impact resistance excellently.

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The above and other objects and advantages of the invention will become more apparent from the following detailed description.

[Means of Solving the Problems and Effect thereof]

The present invention provides a propylene random copolymer comprising a propylene component and an α-olefin component having 4 to 12 carbon atoms, characterized in that

A)   the composition is 40 to 90 mol % of the propylene component and 10 to 60 mol % of the α-olefin component,

B)   the intrinsic viscosity [η] when measured in decalin at 135°C is in the range of 0.5 to 6 dl/g,

C)   the molecular weight distribution ($\bar{M}w/\bar{M}n$) when measured by gel-permeation chromatography (GPC) is in the range of 3 or below,

D)   the melting point [Tm] measured with a differential scanning calorimeter is in the range of 40 to 140°C,

E)   the crystallinity measured with a differential scanning calorimeter is in the range of 1 to 50%,

F)   the content [W_1 wt%] of the component soluble in boiling methyl acetate is in the range of 1 wt% or below,

G)   the content [W_2 wt%] of the component soluble in a mixture solvent of acetone and n-decane (volume ratio 1/1) at 10°C is in the range of $4 \times [\eta]^{-1.2}$ wt% or below,

H)   no signal based on two consecutive methylene chains is observed between two adjacent tertiary carbon atoms in the

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main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer, and

t) the standard deviation of the composition distribution in the copolymer is in the range of 10 mol% or below;

and a modifier for thermoplastic resins which comprises the above propylene random copolymer.

In the composition (A) of the propylene random copolymer of the invention, the propylene component is contained in the amount of 40 to 90 mol%, preferably 50 to 90 mol%, and the α-olefin having 4 to 12 carbon atoms is contained in the amount 10 to 60 mol%, preferably 10 to 50 mol%. When the content of the propylene component exceeds 90 mol% and that of the α-olefin component falls below 10 mol%, the transparency of the copolymer drops.

Examples of the α-olefin having 4 to 12 carbon atoms constituting the propylene random copolymer of the invention are 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene and 1-dodecene.

The intrinsic viscosity [η] (B) of the propylene random copolymer of the invention measured in decalin at 135°C is in the range of 0.5 to 6 dl/g, preferably 1 to 5 dl/g. This characteristic value is an index representing the molecular weight of the propylene random copolymer of the invention, serves to provide the copolymer with the above-mentioned excellent properties together with other characteristic values.

The molecular weight distribution ($\bar{M}w/\bar{M}n$) (C) of the propylene random copolymer of the invention measured by gel-permeation chromatography (GPC) is 3 or below, preferably 2.8 or below, more preferably 2.5 or below. Since the conventionally proposed propylene random copolymers have a $\bar{M}w/\bar{M}n$ value of 3 or higher, the molecular distribution cannot be regarded as sufficiently narrow, low-molecular-weight polymer components co-existing. Therefore the surface non-adhesiveness is poor and blocking is caused thereby. This characteristic value serves to provide the copolymer with the above-mentioned excellent properties together with other characteristic values.

The $\bar{M}w/\bar{M}n$ was measured in accordance with "Gel-Permeation Chromatography" by Takeuchi published by Maruzen, as follows:

(i) Using standard polystyrene whose molecular weight is known (monodisperse polystyrene manufactured by Toyo Soda), its molecular weight M and Gel Permeation Chromatography count were measured to obtain a correlogram between the molecular weight and elution volume (EL). The concentration was 0.02 wt%.

(2) Gel Permeation Chromatograph of a sample was measured by Gel Permeation Chromatography (GPC) and its number-average molecular weight $\bar{M}n$ and weight-average molecular weight $\bar{M}w$ were calculated in terms of polystyrene to obtain

$\overline{M}w/\overline{M}n$. The conditions for preparing the sample and for the GPC measurement were as follows:

[Preparation of Sample]

(a) The sample was dispensed in a conical flask together with o-dichlorobenzene solvent to have a concentration of 0.1 wt%.

(b) In the conical flask containing the sample, 2,6-di-tert-butyl-p-crezol, anti-aging agent, was added in an amount of 0.05 wt% to the polymer solution.

(c) The conical flask was heated to 140°C and stirred for 30 minutes for dissolution.

(d) The mixture was filtered and then subjected to GPC.

[GPC conditions]

(a) Apparatus : manufactured by Waters (150C-ALC/GPC)

(b) Column : manufactured by Toyo Soda (GMH type)

(c) Amount of Sample : 400μl

(d) Temperature : 140°C

(e) Flow rate : 1ml/min

The melting point [Tm] (D) of the propylene random copolymer measured with the differential scanning calorimeter (sometimes referred to as DSC m.p. hereafter) is in the range of 40 to 140°C, preferably 50 to 130°C. The existence of the DSC m.p. is an index representing crystallinity of the copolymer distinguished from the conventional non-crystalline propylene copolymers, serving to provide the copoly-

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mer with the aforesaid excellent properties together with other characteristic values. The DSC m.p. is the maximum endothermic peak temperature (T_m) obtained by allowing a specimen to stand at 200°C for 5 minutes, then cooling it to 20°C at a speed of 20°C/min, allowing it at 20°C for 5 minutes and measuring from 20 to 200°C at 10°C/min.

The crystallinity (E) of the propylene random copolymer of the invention measured with the differential scanning calorimeter is in the range of 1 to 50%, preferably 5 to 40%. This characteristic value is an index representing that the copolymer is excellent in tensile properties, serving to provide the copolymer with the aforesaid excellent properties together with other characteristic values. The crystallinity is calculated using DSC chart on the melting point measured by the above-mentioned method. That is, the specific heat curve (in a temperature range of 160 to 200°C) of the copolymer in complete fusion is extrapolated to lower temperatures to obtain a baseline. And then, the fusion calorie (cal/g) is calculated with the baseline. Next, the fusion calorie is divided by the fusion calorie of propylene crystal per unit (50cal/g) (J. Apply. Poly Sci., 8, 2723 (1964))) to obtain crystallinity (wt%).

In the propylene random copolymer of the invention, the content [W_1 wt%] (F) of the component soluble in boiling methyl acetate is 1 wt% or below, for example, 0.01 to 1 wt%, preferably 0.02 to 0.5 wt%, and more preferably 0.03 to

0.3 wt% with respect to the weight of the copolymer. This characteristic value is an index representing the content of the low-molecular-weight component in the propylene random copolymer of the invention and indicating the width of the composition and molecular weight distributions of the copolymer. Conventionally proposed propylene random copolymers contain a lot of component soluble in boiling methyl acetate, are poor in surface non-adhesiveness and therefore often cause blocking. This characteristic value serves to provide the copolymer with the aforesaid excellent properties together with other characteristic values. The content of the component soluble in boiling methyl acetate was measured as follows: A sample of a small sheet of about 1mm X 1mm X 1mm was put in a cylinder glass filter and extracted with Soxhlet extractor at a reflux frequency of about once/5min for 7 hours. The extract residue was dried with a vacuum dryer (vacuum degree being 10mmHg or lower) until the constant weight was observed, and then was weighed to calculate the weight of the component soluble in boiling methyl acetate from the difference between the weight of the dried residue and the weight of the initial sample. The content (W_1) of the component soluble in boiling methyl acetate was expressed as the percentage of the weight of the component soluble in boiling methyl acetate to that of the initial sample.

In the propylene random copolymer of the invention, the content [W_2 wt%] (G) of the component soluble in a mixture solvent of acetone and n-decane (volume ratio 1/1) at 10°C is 4 X $[\eta]^{-1.2}$ wt% or below, preferably 0.1 X $[\eta]^{-1.2}$ to 3.5 X $[\eta]^{-1.2}$ wt%, more preferably 0.3 X $[\eta]^{-1.2}$ wt% to 3 X $[\eta]^{-1.2}$ wt% ($[\eta]$ is a dimensionless figure of the intrinsic viscosity of the copolymer). This characteristic value represents the content of a low-molecular-weight polymer component in the propylene random copolymer of the invention and an index indicating the width of the composition and molecular weight distributions of the copolymer. Conventionally known propylene random copolymers contain a lot of component soluble in the mixture solvent of acetone and n-decane, are poor in surface non-adhesiveness and therefore often cause blocking. This characteristic value serves to provide the copolymer with the aforesaid excellent properties together with other characteristic values. According to the invention, the content of the component soluble in the mixture solvent was determined as follows: In a 150 milliliter flask with a stirring blade, 1g of a sample of the copolymer, 0.05g of 2,6-di-tert-butyl-4-methylphenol and 50ml of n-decane were put and made into solution in oil bath at 120°C. The mixture was allowed to cool at room temperature for 30 minutes after dissolution. Then 50ml of acetone was added in 30 seconds to the mixture, which was then cooled in water bath at 10°C for 60 minutes.

The precipitated copolymer and the solution containing the low-molecular polymer component were filtered and separated with a glass filter. The solution was dried under 10mmHg at 150°C until the constant weight was observed and then weighed to obtain the content of the component soluble in the mixture solution as the percentage to the weight of the sample of the copolymer. Additionally, in the above determination, the mixture was continuously stirred from the dissolution to just before the filtration.
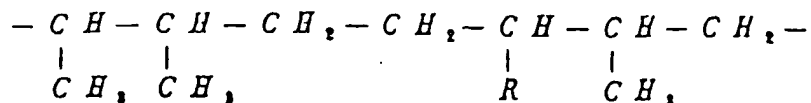
In arrangement (H) of the propylene component and α-olefin component having 4 to 12 carbon atoms in the propylene random copolymer of the invention, no signal is observed which is based on two consecutive methylene chains between two adjacent tertiary carbon atoms in the main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer. To explain it further in detail, when the propylene and the other α-olefin component are copolymerized with the following structure:

$$- C H_2 - C H - C H_2 - C H - C H_2 - C H -$$
$$\qquad\quad | \qquad\qquad\quad | \qquad\qquad\quad |$$
$$\qquad\quad C H_3 \qquad\qquad R \qquad\qquad R$$
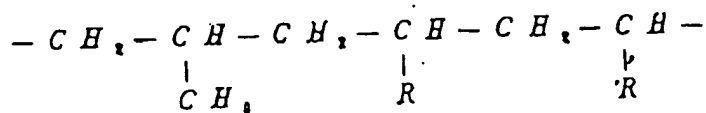
, a signal attributable to a separate methylene group is observed but a signal attributable to two consecutive methylene chains is not observed, between two adjacent tertiary carbon atoms. This indicates that, when the propylene and

the other α-olefin component are copolymerized. both of the components are arranged with regular head-to-tail bonding.

On the contrary, when the propylene and the other α-olefin component are copolymerized with the following structure:

$$-CH - CH - CH_2 - CH_2 - CH - CH - CH_2 -$$
$$\quad | \qquad | \qquad\qquad\qquad\qquad | \qquad |$$
$$\quad CH_3 \quad CH_3 \qquad\qquad\qquad R \quad CH_3$$

, the signal attributable to two consecutive methylene chains is observed between two adjacent tertiary carbon atoms. This indicates that there exist head-to-head bonding and tail-to-tail bonding in this copolymer when the propylene component and the α-olefin component having 4 to 12 carbon atoms are copolymerized. Therefore, this signal represents the arrangement of the propylene and α-olefin components having 4 to 12 carbon atoms constituting the propylene random copolymer of the invention. The absence of the signal serves to provide the copolymer with the aforesaid excellent properties together with other characteristic values. Additionally, the measurement of ^{13}C-NMR was carried out on solution of about 200mg of the copolymer in 1ml of hexachlorobutadiene in a sample tube of 10mm ϕ, usually at 120°C at a measurement frequency of 25.05MHZ, spectral width of 1500HZ, filter width 1500HZ, pulse spacing of 4.2 seconds, pulse width of 7 μ seconds and 2,000 to 5,000 integrating times.

Spectrum was analyzed in accordance with L.P.Lindeman, Anal. Chem., 43, 1245 (1971), J.C.Randall, Macromolecular, 11, 592 (1978) and the like.

The standard deviation δ (I) for the content of propylene in the propylene random copolymer of the invention is, for example, 10 mol% or below, preferably 5 mol% or below. the standard deviation δ is an index indicating randomness of the propylene random copolymer and a copolymer meeting the characteristic values (A) and (H) together with (I) exhibits better properties. The standard deviation δ (I) of the propylene random copolymer of the invention was calculated on the basis of composition distribution of the copolymer with the following formula. The composition distribution was determined by extraction column fractionation wherein extraction temperature was changed stepwise by 5°C from 0 to 130°C with p-xylene solvent, and extraction at a fixed temperature was carried out using p-xylene 21 with respect to 10g of a sample of the copolymer for 4 hours.

$$\sigma = \left[\int_{0}^{100} (\bar{x} - x)^2 f(x) \, dx \right]^{1/2}$$

, wherein $\bar{x}$ is an average content of propylene in the copolymer (mol%), x is a content of propylene (mol%) and f(x) is a differential weight fraction of the component having the content of propylene x (mol%).

The propylene random copolymer of the invention meets the characteristic values specified in the above (A) to (I). Further, preferred copolymer meets at least any one of the characteristic values specified in the following (J) to (N).

Of the propylene random copolymer of the invention, stress at break (J) measured in accordance with JIS (Japanese Industrial Standard) K6301 is 100kg/m^2 or more, preferably 130 to 500kg/cm^2, more preferably 150 to 400kg/cm^2. Elongation at break measured in accordance with JIS K6301 is 400% or more, preferably 450 to 1000%. The stress at break (J) and the elongation at break (K) of the propylene random copolymer of the invention were measured in accordance with tensile testing of JIS K6301. That is, the measurement is performed using as a sample an annular specimen of inside diameter of 18mm and outside diameter of 22mm cut out of a pressed sheet of thickness of mm formed according to JIS K6758, under atmosphere at 25°C at a stress rate of 500mm/min.

Torsional rigidity modulus (L) of the propylene random copolymer of the invention measured by JIS K6745 is, for example 500 to 2,500kg/cm^2, preferably 600 to 2,000kg/cm^2. The measurement of the torsional rigidity modulus is performed using as a sample a strip specimen cut out of a pressed sheet of thickness of 1mm formed according to JIS K6758, under atmosphere at 25°C at a torsion angle of 50°.

Haze value (M) of the propylene random copolymer of the

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invention measured by JIS K6714 is, for example, 25% or less, preferably 20% or less, more preferably 15% or less.

The measurement of Haze value is performed using a sheet of thickness of 1mm formed according to JIS K6758.

JIS C hardness (N) of the propylene random copolymer of the invention measured in accordance to JIS K6701 is usually 60 to 100. The measurement was performed using a sheet of thickness of 3mm formed according to JIS K6758.

In the propylene random copolymer of the invention, another α-olefin, e.g., ethylene, may be copolymerized in a small amount as long as the aforesaid properties are not adversely affected.

The propylene random copolymer of the invention may be prepared by copolymerizing a necessary amount of propylene and α-olefin having 4 to 12 carbon atoms in the presence of a catalyst composed of

(A) a zirconium compound having as ligand at least two indenyl groups, substituted indenyl groups or partially hydrogenated groups thereof which are bonded by ethylene and

(B) aluminoxane.

Examples of the above zirconium compound are ethylene-bis(indenyl)dimethylzirconium, ethylenebis(indenyl)diethyl-zirconium, ethylenebis(indenyl)diphenylzirconium, ethylene-bis(indenyl)methylenezirconium monochloride, ethylene-bis(indenyl)ethylzirconium monochloride, ethylenebis(inde-

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nyl)methylzirconium monobromide, ethylenebis(indenyl)zirco-
nium dichloride, ethylenebis(indenyl)zirconium dibromide,
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethylzirconium,
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methylzirconium
monochloride, ethylenebis(4,5,6,7-tetrahydro-1-
indenyl)zirconium dichloride, ethylenebis(4,5,6,7-tetrahy-
dro-1-indenyl)zirconium dibromide, ethylenebis(4-methyl-1-
indenyl)zirconium dichloride, ethylenebis(5-methyl-1-
indenyl)zirconium dichloride, ethylenebis(6-methyl-1-
indenyl)zirconium dichloride, ethylenebis(7-methyl-1-
indenyl)zirconium dichloride, ethylenebis(5-methoxy-1-
indenyl)zirconium dichloride, ethylenebis(2,3-dimethyl-1-
indenyl)zirconium dichloride, ethylenebis(4,7-dimethyl-1-
indenyl)zirconium dichloride, ethylenebis(4,7-dimethoxy-1-
indenyl)zirconium dichloride.

The aluminoxane (B) used as a catalytic component in
the invention are, for example, organic aluminum compounds
represented by the formula (I) or (II)

$$R_2 Al \left(O Al \right)_m O Al R_2$$
$$\quad\quad\quad \underset{R}{|}$$

[I]

$$\left(O Al \right)_{m+2}$$
$$\quad \underset{R}{|}$$

[II]
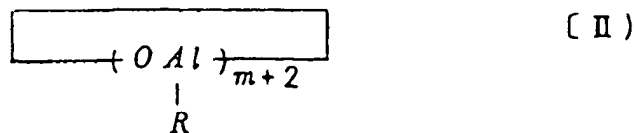
, wherein R is a hydrocarbon group and m is an integer
of 2 or more, preferably 20 or more. In the above aluminox-

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ane, R is a hydrocarbon group such as methyl, ethyl, propyl and butyl, preferably methyl and ethyl, more preferably methyl and m is an integer of 2 or more, preferably 20 or more, more preferably 25 to 100. The aluminoxane is prepared by, for example, the following processes:

(1) Trialkylaluminum is added to and reacted with suspension in hydrocarbon medium of a compound containing absorbed water, salt containing water of crystallization, e.g., magnesium hydrate, copper sulfate hydrate, and aluminum sulfate hydrate.

(2) Water is allowed to act directly on trialkylaluminum in a medium, e.g., of benzene, toluene, ethyl ether or tetrahydrofuran.

Of the above two methods, method (1) is preferably used. Additionally, the aluminoxane may contain a small amount of organometallic component.

The invention is based on the finding that a copolymer which has never been proposed is obtained by copolymerizing propylene and α-olefin having 4 to 12 carbon atoms in a specific ratio using such a catalyst as mentioned above. Propylene and the α-olefin may be copolymerized both in liquid phase and in gas phase, though liquid phase copolymerization is preferred. The copolymerization in liquid phase is usually performed in a medium of hydrocarbon. Examples of the hydrocarbon medium are aliphatic hydrocar-

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bons such as pentane, hexane, heptane, octane and decane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzen, toluene and xylene; petroleum fractions such as gasoline, kerosine and gas oil; and also olefins, very materials for the copolymer, among which the aromatic hydrocarbons are preferred. The usage ratio of the zirconium compound when the inventive method is carried out in liquid phase is usually 10^{-7} to 10^{-2} gram atom/l, preferably 10^{-6} to 10^{-3} gram atom/l in terms of concentration of zirconium metal atom in copolymerization system. The usage ratio of the aluminoxane is usually 10^{-4} to 10^{-1} gram atom/l, preferably 10^{-3} to 5×10^{-2} gram atom/l in terms of concentration of the aluminum atom in copolymerization system. The ratio of aluminum atom to zirconium metal atom in the polymerization system is usually 20 to 10^6, preferably 50 to 10^5.

The copolymerization of the invention may be carried out in a way similar to conventional polymerization of olefins with Ziegler catalyst. Preferably, copolymerization temperature is selected from a range of -80 to 50, preferably -60 to 30. The polymerization is preferably carried out at elevated pressure, usually at atmospheric pressure to $20kg/cm^2$, preferably at 2 to $15kg/cm^2$. Materials supplied to the polymerization system are a mixture of propylene and α-olefin. The content of propylene in the polymerization materials is usually 30 to 88 mol%, preferably 35 to 85

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mol%, and the content of the α-olefin in the polymerization material olefins is usually 12 to 70 mol%, preferably 15 to 65 mol%. The molecular weight of the copolymer may be controlled by hydrogen and/or polymerization temperature and further by the usage ratio of the catalytic component. The propylene random copolymer of the invention is distinctive from conventional ones in that it is non-adhesive and good in transparency and has other various properties already discussed. The copolymer may be made into a film, sheet, hollow container or other various articles so as to serve for various application, by conventional methods such as extrusion, blow molding, injection molding, pressing and vacuum forming. Especially, the copolymer is suitable for films for wrapping since it is excellent in transparency, blocking resistance, heat-sealing properties and flexibility. Also the copolymer is aptly used as films for protecting metal or the like due to its aforesaid properties.

In forming, a variety of stabilizer, anti-oxidant, UV absorber, antistat, lubricant, plasticizer, colorant, and organic or inorganic filler may be added. Examples of such additives are 2,6-di-tert-butyl-p-crezol, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] methane, 4,4'-butelidene(?)bis(6-tert-butyl-m-crezol), tocopherols, ascorbic acid, dilaurylthiodipropionate, phosphorus stabilizer, fatty acid monoglyceride, N,N-(bis-2-

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hydroxyethyl)alkylamine, 2-(2'-hydroxy-3',5'-di-tert-butyl-phenyl)-5-chlorobenzotriazole, calcium stearate, magnesium oxide, magnesium hydroxide, alumina, aluminum hydroxide, silica, hydrotalcite, talc, clay, gypsum, glass fiber, titania, calcium carbonate, carbon black, petroleum resin, polybutene, wax, and synthetic or natural rubber.

The copolymer of the invention may be used as mixture with other thermoplastic resin. Examples thereof are poly-ethylene of high, medium or low density, polypropylene, poly-1-butene, poly-4-methyl-1-pentene, ethylene · vinyl acetate copolymer, surlyn A, ethylene · vinyl alcohol copol-ymer, polystyrene and maleic acid anhydride graft thereof.

The propylene random copolymer of the invention may be blended as modifier to a variety of thermoplastic resins to enhance impact resistance, low-temperature impact resist-ance, flex resistance, transparency, and low-temperature heat sealing properties. Examples of the thermoplastic resins are other ethylene polymers containing ethylene as major component, crystalline olefin polymers other than the ethylene polymers and engineering resins.

The propylene random copolymer of the invention may be blended with ethylene polymer containing ethylene as major component such as polyethylene so as to enhance impact resistance, low-temperature impact resistance, flex resist-ance, transparency, and low-temperature heat sealing proper-ties of articles formed of the ethylene polymer. The above

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ethylene polymer include polyethylene of high density, polyethylene of medium density, polyethylene of low density, and copolymers of ethylene as major component and α-olefin having 3 to 20 carbon atoms such as propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eucosene. The intrinsic viscosity [η] thereof measured in decalin at 135°C is usually 0.5 to 20 dl/g.

The blending ratio of the propylene random copolymer of the invention with the ethylene polymer is usually 1 to 100 parts by weight, preferably 2 to 60 parts by weight, with respect to 100 parts by weight of the ethylene polymer. To the obtained ethylene polymer composition, if necessary, various additives such as anti-oxidant, hydrochloric acid absorbent, antiflocculant, heat-resistant stabilizer, UV absorbent, lubricant, weathering agent, antistat, nucleating agent, colorant and filler may further be added. The blending ratio may be suitably set. The ethylene polymer composition may be prepared by a conventional method.

The propylene random copolymer of the invention may also be blended with crystalline olefin polymer other than the above-mentioned ethylene polymer so as to enhance impact resistance, especially low-temperature impact resistance of articles formed of the olefin polymer. Also films of good blocking resistance, transparency and heat-sealing proper-

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ties may be obtained. Examples of the crystalline olefin polymer other than the ethylene polymer are polypropylene, poly-1-butene, poly-4-methyl-1-pentene, and also crystalline α-olefin copolymers of α-olefin (α1) such as propylene, 1-butene and 1-hexene and α-olefin (α2) having 2 to 20 carbon atoms which is different from the α-olefin (α1) such as ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene, for example, propylene • ethylene copolymer and 1-butene • ethylene copolymer. The intrinsic viscosity [η] of the crystalline olefin polymer measured in decalin at 135°C is usually 0.5 to 10 dl/g. The crystallinity thereof is 5% or more, preferably 20% or more.

The blending ratio of the propylene random copolymer of the invention with the crystalline olefin polymer is usually 1 to 100 parts by weight, preferably 2 to 60 parts by weight, with respect to 100 parts by weight of the crystalline olefin polymer. To the crystalline olefin polymer composition, if necessary, various additives such as antioxidant, hydrochloric acid absorbent, antiflocculant, heat-resistant stabilizer, UV absorbent, lubricant, weathering agent, antistat, nucleating agent, colorant and filler may be added. The crystalline α-olefin polymer composition may be prepared by a conventional method.

Further the propylene random copolymer of the invention may be blended with various engineering resins so as to

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improve properties of the engineering resins such as impact resistance and sliding properties. When the engineering resin has a polar group, the propylene random copolymer of the invention is preferably prepared into a modified propylene random copolymer by graft-copolymerization with an unsaturated carboxylic acid such as maleic acid, citraconic acid, itaconic acid, maleic anhydride, citraconic anhydride, itaconic anhydride, dimethyl maleate, dimethyl citranate and dimethyl itaconate or a derivative thereof, in order to improve its affinity with and diffusion into the engineering resin. The graft ratio of the unsaturated carboxylic acid or a derivative thereof is usually 0.02 to 50 parts by weight with respect to 100 parts by weight of the propylene random copolymer. Examples of the engineering resin are polyesters such as polyethylene terephthalate and polybutylene terephthalate, polyamides such as hexamethyleneadipamide, octamethyleneadipamide, decamethyleneadipamide, dodecamethyleneadipamide and polycaprolactam, polyaryleneoxides such as polyphenyleneoxide, polyacetal, ABS, AES, and polycarbonate. The blending ratio of the propylene random copolymer or a modified copolymer thereof with the engineering resin is usually 0.2 to 20 parts by weight with respect to 100 parts by weight of the engineering resin. To the engineering resin composition, if necessary, various additives such as anti-oxidant, hydrochloric acid absorbent,

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antiflocculant, heat-resistant stabilizer, UV absorbent, lubricant, weathering agent, antistat, nucleating agent, colorant and filler may be added. The engineering resin composition may be prepared by a conventional method.

The propylene random copolymer of the invention may be blended with various rubber-like polymers to improve properties of the rubber-like polymers such as chemical resistance and rigidity. Examples of the rubber-like polymers are ethylene · propylene · unconjugated diene copolymer, ethylene · 1-butene · unconjugated diene copolymer, polybutadiene rubber, polyisoprene rubber and stylene · butadiene · stylene block copolymer. The blending ratio of the propylene random copolymer is usually 1 to 100 parts by weight with respect to 100 parts by weight of the rubber-like polymer. To the rubber-like polymer composition, if necessary, various additives such as filler, crosslinker, crosslinking assistant, colorant and stabilizer may be added. The rubber-like polymer composition may be prepared by a conventional method.

[Example]

The present invention will be further explained by way of examples.

Example 1

Preparation of ethylene · bis(indenyl)zirconium dichloride

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In a 400-milliliter glass flask wherein atmosphere was sufficiently replaced with nitrogen, 100ml of tetrahydrofuran were put and cooled to -195°C. Then 8.2g of zirconium tetrachloride were added and heated gradually to room temperature to obtain suspension. Then 35 millimol of lithium salt of bis(indenyl)ethane dissolved in 80 ml of tetrahydrofuran [ref. J.Organometal.chem. 232, 233(1982)] were added and stirred at 20°C for 2 hours. Then hydrogen chloride gas was blown in for several seconds, and immediately tetrahydrofuran and hydrogen chloride gas were removed at reduced pressure to obtain a solid product. The solid product was washed with 10% aqueous hydrochloric acid, ethanol and diethyl ether and dried at reduced pressure. Ethylenebis(indenyl)zirconium dichloride (4.9g) was obtained.

Preparation of Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride

In a 1-liter stainless autoclave, 4.5g of the ethylene-bis(indenyl)zirconium dichloride obtained above, 300mg of platinum (IV) oxide and 100ml of dichloromethane were put and hydrogen was introduced to 100kg/cm^2·G. The reaction mixture was transferred into 1 liter of dichloromethane. Then platinum (IV) oxide was separated away by filtration and dichloromethane was removed to obtain a solid product. The solid product was washed with petroleum ether and then

recrystallized with hot toluene to obtain 2.9g of ethylene-
bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride.

Preparation of methylaluminoxane

In a 2-liter glass flask wherein atmosphere was suffi-
ciently replaced with argon, 70g of $MgCl_2 \cdot 6H_2O$ and 625ml of
toluene were put and cooled to 0°C. Then 1.25 mol of tri-
methylaluminum diluted with 625ml of toluene were dropped.
After the dropping, the mixture was heated to 60°C and
allowed to react at the same temperature for 96 hours.
After the reaction, the reaction mixture was separated into
solid and liquid by filtration and the liquid was used as
aluminoxane solution for polymerization. Part of the liquid
was used as a sample for determination of molecular weight
after removing toluene. The molecular weight determined by
cryoscopy with benzene was 1570. The aluminoxane had m
value of 25.

Polymerization

In a stainless autoclave having an internal volume of
100 liters wherein atmosphere was sufficiently replaced with
nitrogen, 25 liters of refined toluene, 10kg (238 mol) of
propylene and 7.2kg (129 mol) of 1-butene were put at
-150°C, and then methylaluminoxane in the amount correspond-
ing to 550 milligram atom in terms of aluminum atom and
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichlo-
ride in the amount corresponding to 0.55 milligram atom in

terms of zirconium atom were put. The mixture was polymer-
ized at -15°C for 12 hours. A small amount of methanol was
added to stop the polymerization, and the mixture was purged
of unreacted propylene and 1-butene. Further, catalyst
residue was removed with warm water containing a small
amount of hydrochloric acid and methanol, and then the
polymerization mixture was put in a large amount of methanol
to precipitate polymer. The precipitated polymer was washed
with methanol and dried at reduced pressure at 100°C for a
whole day and night. Thus 1190g of copolymer was obtained.
The content of propylene in the copolymer determined by
^{13}C-NMR was 68.6 mol%, [η] was 2.03dl/g, $\overline{Mw}/\overline{Mn}$ determined
by GPC was 2.21, the melting point and crystallinity deter-
mined by DSC were 93°C and 16% respectively, the content
soluble in boiling methyl acetate is 0.12 wt%, the content
soluble in the mixture solvent of acetone · n-decane is
0.25wt%, and the standard deviation of the content of pro-
pylene determined by composition fractionation was 1.1 mol%.

The stress at break and elongation at break measured in
accordance with JIS K6301 was 220kg/cm^2 and 720% respective-
ly, and the haze (according to JIS K6714), the torsional
rigidity modulus and C rigidity of a sheet of thickness of
1mm formed in accordance with JIS K6758 was 5%, 900kg/cm^2
and 61 respectively. No signal based on two consecutive
methylene chains was observed between two adjacent tertiary

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carbon atoms in the main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer.

Examples 2 to 4 and Comparative Example 1

Polymerization was carried out as in Example 1 except that the ratio of propylene and 1-butene to be supplied, the polymerization temperature and period were changed. No signal based on two consecutive methylene chains was observed between two adjacent tertiary carbon atoms in the main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer. The results are shown in Table 1.

Example 5

Polymerization was carried out as in Example 1 except that ethylenebis(indenyl)zirconium dichloride as obtained in Example 1 was used in the amount corresponding to 0.60 milligram atom in terms of zirconium atom and polymerization conditions shown in Table 1 were used. No signal based on two consecutive methylene chains was observed between two adjacent tertiary carbon atoms in the main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer. The results are shown in Table 1.

Examples 6 and 7

Polymerization was carried out as in Example 1 except that 1-hexene or 4-methyl-1-pentene was used instead of 1-butene and polymerization conditions shown in Table 1 were

used. No signal based on two consecutive methylene chains was observed between two adjacent tertiary carbon atoms in the main chain of the copolymer in the ^{13}C-NMR spectrum of the copolymer. The results are shown in Table 1.

Comparative Example 2

In a stainless autoclave having an internal volume of 20 liters, 5kg (119 mol) of propylene and 3.6kg (64 mol) of 1-butene were put at room temperature and hydrogen was introduced so that partial hydrogen pressure in the auto-clave became 1.5kg/cm^2. Then diethylaluminum chloride in the amount corresponding to 20 milligram atom in terms of aluminum atom and titanium trichloride (TAC-141 manufactured by Toho Titanium) in the amount corresponding to 10 milli-gram atom in terms of titanium atom were put in the auto-clave to start polymerization. The polymerization was at 60°C for 1 hour. The following steps were carried out as in Example 1. Thus 790g of copolymer were obtained. Proper-ties of the copolymer are shown in Table 1.

Example 8

Polymerization was carried out as in Example 6 except that 1-decene was used as α-olefin. Copolymer (730g) was obtained which contained 89.2 mol% propylene, had an intrin-sic viscosity of 1.63dl/g, $\overline{M}w/\overline{M}n$ of 2.44, melting point of 112°C and crystallinity of 22%, 0.13 wt% content soluble in boiling methyl acetate, 0.25 wt% content soluble in acetone

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n-decane, and a standard deviation of 1.4 mol%. Its
stress at break was 240kg/cm^2, elongation at break was 650%,
torsional rigidity modulus was 1100kg/cm^2, haze was 7% and
hardness was 84.

Application Example 1

Making of a polypropylene composite film

Propylene random copolymer [P-1] as obtained in Example
1 and crystalline propylene · ethylene random copolymer [P-
2] (content of ethylene : 4.0 mol%, intrinsic viscosity :
2.1dl/g, DSC melting point : 147°C) were melted and mixed in
a ratio of 30/70 and this composition was supplied to a
two-layer film die at a resin temperature of 240°C, while
crystalline polypropylene (intrinsic viscosity : 2.0dl/g,
isotactic index : 97%) to form a substrate layer was melted
in another extruder and supplied to the die at a resin
temperature of 240°C to be co-extruded from the die, thereby
a polypropylene composite film being formed which was com-
posed of a substrate layer (40μ) of the crystalline poly-
propylene and a layer (10μ) of the crystalline propylene
random copolymer. Blocking resistance, haze, scratch re-
sistance, heat sealing properties of the composite film were
evaluated as follows:

(1) Blocking resistance

measured in accordance with ASTM D1893

(2) Haze

measured in accordance with ASTM D1003

(3) Scratch resistance

The surface of the polypropylene composite film on
which the crystalline propylene random copolymer composition
was disposed was put on the surface of another polypropylene
composite film on which crystalline propylene random copoly-
mer composite was disposed, and rubbed 15 times with a 5-
kilogram iron block as load. Then the haze was measured by
the method (1) and the difference (Δ haze) between this haze
and the haze before the robbing was calculated as scratch
resistance.

(4) Heat-sealing properties

The surface of the polypropylene composite film on
which the crystalline propylene random copolymer composite
was disposed was put on the surface of another polypropylene
composite film on which the crystalline propylene random
copolymer composite was disposed, heat-sealed with a sealing
bar of 5mm in width at a pressure of 2kg/cm^3 for 1 second
with varying the temperature, and then allowed to cool. A
specimen of 15mm in width was cut out of the sealed films
and the sealed portion thereof was peeled off at a cross
head speed of 200mm/min to obtain the strength. The results
are shown in Table 2.

Application Example 2

The same procedure as in Application Example 1 was

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repeated except that the mixture ratio of [P-1] to [P-2] was set to be 20/80. Results are shown in Table 2.

Application Example 3

The same procedure as in Application Example 1 was repeated except that crystalline propylene · ethylene 1-butene random copolymer containing 3.4 mol% ethylene and 1.9 mol% 1-butene of intrinsic viscosity of 2.1dl/g and DSC melting point of 139°C was used as [P-2] and the mixture ratio of [P-1] to [P-2] was set to be 10/90. Results are shown in Table 2.

Comparative Application Example 1

The same procedure as in Application Example 1 was repeated except that only [P-2] used in Application Examples 1 and 2 was used to form a film. Results are shown in Table 2.

Comparative Application Example 2

The same procedure as in Application Example 1 was repeated except that only [P-2] used in Application Example 3 was used to form a film. Results are shown in Table 2.

Comparative Application Example 3

The same procedure as in Application Example 1 was repeated except that the propylene random copolymer as obtained in Comparative Example 2 was used as [P-1]. Re-

sults are shown in Table 2.

[Effect of Invention]

As described above, the propylene random copolymer of the invention has narrow molecular and composition distributions, exhibits excellent transparency, surface non-adhesiveness and low crystallinity.

The copolymer of the invention can be blended with a thermoplastic resin to enhance various characteristics of the resin.

Table 1

	Supplied Gas α-Olefin	Propylene*/α-Olefin (molecular ratio)	Polimerization Temperature (°C)	Polimerization Period (hr)	Yield of Co-polymer (g)	Content of Propylene (mol%)	Intrinsic Viscosity[η] (dl/g)	$\bar{M}w/\bar{M}n$	Melting Point Tm (°C)
Example 1	1-butene	65/35	-15	12	1190	68.6	2.03	2.21	93
2	1-butene	55/45	-10	8	1100	57.0	1.50	2.15	78
3	1-butene	45/55	-15	12	1040	49.0	1.75	2.38	60
4	1-butene	75/25	-10	6	1230	77.9	1.61	2.13	109
5	1-butene	65/35	-10	16	1120	70.1	1.55	2.28	96
6	1-hexene	60/40	-15	16	830	86.3	1.70	2.35	117
7	4MP-1**	55/45	-15	16	720	87.1	1.63	2.41	123
Comparative Example 1	1-butene	90/10	-10	5	1320	95.4	1.77	2.15	141
2	1-butene	65/35	60	1	790	67.5	1.89	7.15	60,107

* Supply amount of Propylene = 10kg (except 5kg for Comparative Example 2)
** 4MP-1 : 4-methyl-1-pentene

Table 1 (continued)

	Crystallinity (%)	Content soluble in boiling methyl acetate (wt%)	Content soluble in Aceton·n-decane (wt%)	Standard Deviation (mol%)	Stress at break (kg/cm²)	Elongation at break (%)	Torsional rigidity modulus (kg/cm²)	Haze (%)	Hardness (JIS C)
Example 1	16	0.12	0.25	1.1	220	720	900	5	81
2	13	0.13	0.30	1.1	170	750	700	4	75
3	7	0.15	0.35	1.2	230	650	800	2	68
4	21	0.10	0.20	1.4	225	690	1400	6	67
5	17	0.11	0.25	1.3	200	700	1000	5	82
6	26	0.11	0.25	1.4	280	600	-	11	69
7	23	0.13	0.30	1.6	260	610	-	12	65
Comparative Example 1	32	0.04	0.10	1.1	250	600	2200	25	68
2	23	3.5	5.9	14.5	170	750	500	38	64

Table 2

	[P-1]/[P-2] (Blend Ratio)	Blocking Resistance (g/cm)	Haze (%)	Scratch Resistance (%)	Heat Sealing Strength (g/15mm)						
					90°C	100°C	110°C	120°C	130°C	140°C	150°C
Application Example 1	30/70	1.7	1.0	3.9	-	-	-	60	1200	2100	2300
Application Example 2	20/80	1.3	1.0	4.0	-	-	-	-	500	2200	2200
Application Example 3	10/90	0.3	1.2	4.1	-	-	-	-	1000	1500	1800
Comparative Application Example 1	0/100	0.2	2.2	3.9	-	-	-	-	50	800	1800
Comparative Application Example 2	0/100	0.2	2.0	4.0	-	-	-	-	200	800	1600
Comparative Application Example 3	30/70	4.1	2.0	4.8	-	-	-	-	500	1200	1900